# SCIENCE FOR GLASS PRODUCTION

## USE OF SODA PRODUCED BY THE HYDROCHEMICAL METHOD FROM NEPHELINE MATERIAL IN GLASS MELTING

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The corrosive effect of nepheline-based soda on the refractory lining of glass-melting furnaces is tested. The main principle of the process of melting industrial glass from batches containing such soda are discussed. It is established that the use of soda does not provoke complications in glass melting and does not entail the risk of shortening the furnace campaign.

The main raw materials acting as vehicles for introducing sodium oxide into most industrial glasses are soda and sodium sulfate.

As soda has a lower corrosion activity than sodium sulfate, refractory brickwork in furnaces undergoes significantly less destruction in the case of melting pure soda batch (not containing sodium sulfate). However, melting glass from pure soda batch has some significant disadvantages as well. In these conditions the process of clarification is not intense enough. Moreover, there is enhanced probability of formation of loose white flakes in the melting foam zone, which are agglomerations of unmelted quartz grains partly transformed into cristobalite [1]. This is called silica foam, which results in mass-scale rejection of finished glass due to crystalline inclusions. If such agglomerations persist on the surface of the melt mirror for a long time, they may form a continuous crust that is very difficult to remove. The reason for this is that silicate-formation reactions in melting a purely soda batch proceed at relatively low temperatures and all alkali-bearing components participate in the chemical reactions. At the same time, residual (not entering into reactions with other batch components and not dissolved in the melt) quartz sand grains cannot dissolve in the melt due to an absence of free alkalis, whereas intense foam existing in the melting zone carries the unmelted particles onto the melt surface.

It is known that reactions of silicate and glass formation in a soda-sulfate batch are significantly more complicated than in a pure soda batch. Since sodium sulfate enters into a reaction with $SiO_2$ very slowly, to achieve its decomposition according to the reaction

$$Na_2SO_4 + 2C = Na_2S + 2CO_2$$
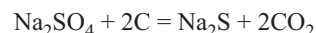
it is necessary to introduce a reducing agent (coal, residual oil) into the batch. The completeness of the sodium sulfate reduction determines the quality of the entire melting process. If reduction is incomplete due to a lack of carbon in the batch (for instance, due to its pre-schedule burning), part of the sodium sulfate remains undecomposed, melts, and floats to the surface of the glass melt in the form of lye. Lye in excessive quantities is extremely aggressive with respect to the refractory brickwork of a glass-melting furnace, which deteriorates the quality of the glass.

If a batch contains sodium sulfate, which decomposes much more slowly than soda does, the amount of alkalis in the upper layers of the glass melt is sufficient to convert the unmelted quartz sand grains into a melt, which virtually excludes the possibility of silica foam formation, which may arise in melting a purely soda batch. This is one of the advantages of soda-sulfate melting.

Introduction of a reducing agent (carbon) in an amount of 7 – 8% of the mass of sodium sulfate in the batch enables one to avoid the formation of excessive lye or foam [2]. Silica foam may also arise under highly reducing melting conditions, for instance, with an overdose of reducing agent, which leads to the complete absence of lye, which, although in small quantities is present in the furnace in melting a sodium sulfate batch.

Another important function of sodium sulfate in the composition of soda-sulfate batch is that of a high-temperature

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**TABLE 1**

| Soda variety | Weight content, %[*] | | | |
|---|---|---|---|---|
| | $Na_2CO_3$ | $K_2CO_3$ | $K_2SO_4$ | NaCl |
| Ammonia (1) | 99.0 | – | – | 0.5 |
| Nepheline: | | | | |
| 2 | 98.9 | 0.6 | 0.4 | – |
| 3 | 98.5 | 0.7 | 0.7 | – |
| 4 | 96.2 | 2.4 | 1.3 | – |

[*] $Fe_2O_3$ content in all compositions was equal to 0.005%.

clarifier, which significantly accelerates the removal of gas inclusions from the glass melt compared to melting a purely soda batch. The reactions between sodium sulfate and silica occur at temperatures of $1300 – 1450°C$ [3] with gas emission according to the reaction

$$Na_2SO_4 + SiO_2 \rightarrow Na_2SiO_3 + SO_2 + \frac{1}{2} O_2.$$
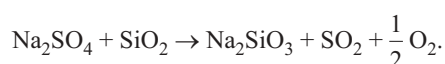
In this case, large gas bubbles in the melt are formed in large quantities and rapidly rise toward the melt surface, entraining smaller bubbles present in the melt, which intensifies the clarification process. Later on, with temperature decreasing along the melting tank length by $20 – 30°C$, the reaction rate of decomposition of $Na_2SO_4$ becomes negligible and no additional bubbles are formed in the melt, although not all of the sodium sulfate has decomposed.

Recently, the use of soda-sulfate batch with a soda : sodium sulfate ratio ranging from 99.5 : 0.5 to 95.0 : 5.0 without adding a reducing agent has become an accepted domestic and international practice. Under these conditions, a slow decomposition of sodium sulfate is provided, mainly due to its reaction with silica, ensuring a high-temperature clarifying effect. At the same time, a reserve of undecomposed sodium sulfate is formed, which is capable of reaction in glass melting with residual unmelted quartz sand grains, which excludes the possibility of silica foam formation.

As a rule, two varieties of soda are used in glass melting. The most widely used is technical soda ash produced using the Solvay ammonia method (hereafter "ammonia soda") and less frequently technical soda ash produced by hydrochemical methods from nepheline raw material, in other words, a soda-potassium mixture (hereafter "nepheline soda").

Ammonia soda, apart from NaCl, virtually does not contain impurities that complicate the glass-melting process. To avoid fast corrosion of the upper refractory brickwork of the furnace, especially its silica brick elements, the content of NaCl should not exceed 0.5%. At the same time, according to GOST 5100–85, the content of NaCl in the product of the second category commonly used by glass factories reaches 0.8%, which sharply increases the corrosion activity of ammonia soda.

Nepheline soda, in which the NaCl that is aggressive to the furnace refractories is totally absent, contains two main impurities: $K_2CO_3$ and $K_2SO_4$. The presence of $K_2CO_3$ does not lead to any technological complications in glass melting. Furthermore, introduction of $1.0 – 1.5\%$ potassium oxides (usually instead of sodium oxide) decreases the propensity of glass for crystallization, improves its molding parameters and color shade, and imparts luster. The presence of $K_2SO_4$ (up to 6.0%) in nepheline soda produces a number of technological complications due to a higher melting point (compared to $Na_2SO_4$), volatility, and aggressiveness to the refractory brickwork of the furnace. It is precisely the high corrosion activity of nepheline soda, which shortens the service life of glass-melting furnaces, that has been the main obstacle to a wider use of this product in the glass industry. Another restraining factor is the large spread in the quality parameters of particular nepheline soda batches [4].

It is known that volatile batch and glass components have the most aggressive effect on silica brick elements of the melting tank brickwork (main roof, arches and walls of the flame space, regeneration chambers walls). To estimate the degree of aggressiveness of various types of soda, testing was organized using the following method. Samples of four soda varieties (each weighing 80 g) were poured into corundum crucibles of 100-ml capacity and 60 mm in diameter: ammonia soda of grade A, category 1 (GOST 5100–85) produced by Sterlitamaksoda JSC, and three varieties of nepheline soda (samples obtained from the Achinskii Alumina Works). The chemical compositions of the specified products are indicated in Table 1.

Crucibles were covered by plates 30 mm thick made of dinas (silica) brick of grade DS (GOST 3910–75), placed into an electric furnace, and exposed for 24 h at a temperature of $1500°C$. After testing, the depth of corrosion and the reaction-zone thickness were measured in samples and the content of alkaline components was determined along the reaction-zone depth. To do this, the samples were cut across, including the reaction zone. The corrosion depth and the refractory-zone thickness were measured in five cross sections, and the chemical composition of the reaction zone was determined on its surface in the site of contact with the intact zone. The averaged experimental results are shown in Fig. 1.

The testing indicated that ammonia soda and two nepheline soda varieties (Table 1, samples 2 and 3) differ insignificantly in the degree of their corrosive effect on dinas refractories. According to numerous industrial reports, the use of ammonia soda in glass melting, provided the service conditions of glass-melting furnaces are optimum, does not lead to active destruction of dinas elements in the melting zone and these elements do not limit the term of the furnace campaign; consequently, it is reasonable to infer that the same holds true for nepheline soda with a $K_2SO_4$ content up to 0.7%. When the nepheline soda used has a higher content of this component (up to 1.3% in our case), elevated corrosive activity of such material is registered, which in industrial conditions may influence the degree of wear of dinas elements in brickwork and to a certain extent have an adverse effect on the furnace campaign duration.

Thus, the use of nepheline soda with a $K_2SO_4$ content up to 0.7% appears quite reasonable.

As for the purely technological aspects of using nepheline soda in glass melting, the most adequate model which can be used to describe with a high degree of accuracy the main specifics of glass melting is a well-studied process of glass melting using a batch prepared from ammonia soda and sodium sulfate.

The expediency of such an approach implying the existence of certain technological analogies in the behavior of ammonia soda – sodium sulfate composition and nepheline soda ($Na_2CO_3 + K_2CO_3 + K_2SO_4$) in glass melting is based on the similarity of the physical and chemical properties of sodium and potassium salts [5]. It is also known that $Na_2O$ and $K_2O$ in an amount of 1 – 3% are completely interchangeable in a glass composition whose properties vary insignificantly. However, the experience in melting glass into which $Na_2O$ is introduced with ammonia soda and partly via sodium sulfate cannot be mechanically extrapolated to a process in which alkali components are introduced into glass via $Na_2CO_3$, $K_2CO_3$, and $K_2SO_4$ contained in nepheline soda. In this case, one should bear in mind that potassium sulfate is a higher-melting and stronger chemical compound than sodium sulfate. The respective melting points of $Na_2SO_4$ and $K_2SO_4$ are 884 and 1071°C [6].

Potassium sulfate contained in nepheline soda, similarly to sodium sulfate, acts as a high-temperature clarifying agent. Since $K_2SO_4$ is more high-melting, this stops its clarifying effect on the melt in a higher temperature interval, and, according to technological estimates, the start and end of this temperature interval are 20 – 30°C higher (for $Na_2SO_4$ this interval is 1300 – 1450°C).

For comparative evaluation (with respect to $Na_2SO_4$) of the efficiency of $K_2SO_4$ in nepheline material as a clarifying additive, the content of $K_2SO_4$ (mass parts) was calculated per 100 mass parts of quartz sand. The calculation was performed for a batch providing for introduction of 72% $SiO_2$ and 14% $Na_2O$ into glass. The specified contents of $SiO_2$ and $Na_2O$ in glass were selected as the mean values of these parameters in actual chemical compositions of most industrial glasses (mainly sheet and container glass), in which the content of $SiO_2$ and $Na_2O$ varies in intervals of 70 – 73 and 13 – 15%, respectively.

In using nepheline soda with a soda : sulfate ratio equal to 99.5 : 0.5 and with an initial $K_2SO_4$ content in the considered soda batches equal to 0.4, 0.7, and 1.3%, respectively, the amount of $K_2SO_4$ per 100 kg of quartz sand in a batch will be 0.15, 0.26, and 0.49 kg, respectively. The amount of sodium sulfate in a batch of the same composition with a soda : sulfate ratio equal to 99.5 : 0.5 will amount to about 0.25 kg per 100 kg of quartz sand.

To ensure a correct correlation of these parameters for $Na_2SO_4$ and $K_2SO_4$, the parameters of $K_2SO_4$ have to be converted to a sodium-sulfate equivalent by multiplying them by a factor equal to 0.82. This coefficient takes into account the fact that the volume of the gaseous phase released (a mixture
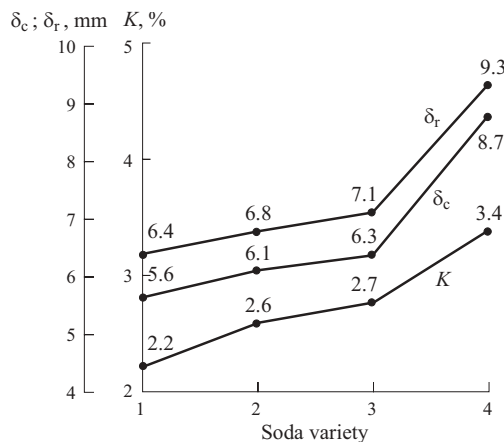


**Fig. 1.** Depth of refractory corrosion $\delta_c$, thickness of the reaction zone $\delta_r$, and content of $R_2O$ in this zone $K$ depending on the variety of soda (see Table 1).

of $SO_2$ and $O_2$) is lower by 18% than the volume of the gaseous phase released in decomposition of $Na_2SO_4$, and this is very significant for accelerating the process of glass-melt clarification. The parameters of $K_2SO_4$ converted to the sodium-sulfate equivalent amount to 0.12, 0.21, and 0.40 kg.

It can be seen from the calculation results that with a content of $K_2SO_4$ in nepheline soda equal to 0.4 and 0.7%, the resource of this component is insufficient for clarification of the glass melt, especially at a level of 0.4% (the quantity of mass parts of $K_2SO_4$ converted to the sodium-sulfate equivalent is lower than the same parameters for $Na_2SO_4$ with a soda : sulfate ratio of 99.5 : 0.5). Consequently, in using nepheline soda with a $K_2SO_4$ content of 0.4 and 0.7%, additional introduction of sodium sulfate is required to reach a level equivalent to at least 0.25 mass parts of $Na_2SO_4$ per 100 mass parts of quartz sand.

Additional introduction of sodium sulfate, due to its lower melting point than that of $K_2SO_4$, will make it possible to begin intensification of the clarification process at a lower temperature (by about 30°C) compared with $K_2SO_4$, which will have a positive effect on the clarification in general due to the extended duration of this process and due to a more rational use of the melting zone surface in the furnace.

When the $K_2SO_4$ content amounts to 1.3%, the potential of this component as a high-temperature clarifier is quite sufficient to ensure efficient clarification of the glass melt, and there is no need to add sodium sulfate.

In introducing 95% sodium oxide via nepheline soda, the amount of potassium sulfate in the batch per 100 kg of quartz sand is equal to 0.12, 0.21, and 0.40 kg (respectively for a content of $K_2SO_4$ in nepheline soda amounting to 0.4, 0.7, and 1.3%). Taking into account the factor of 0.82, these parameters in the sodium-sulfate equivalent decrease to 0.10, 0.17, and 0.33%, respectively. At the same time, with a soda : sulfate ratio equal to 95.0 : 5.0, the quantity of sodium sulfate at the expense of the latter and ammonia soda reaches 2.25 kg per 100 kg of quartz sand, which on the average ex-

ceeds 15 times the content of $K_2SO_4$ in the batch expressed in the sodium-sulfate equivalent. Apparently, to ensure the soda : sulfate ratio equal to 95.0 : 5.0, a substantial sodium-sulfate additive is required to bring the total content of potassium and sodium sulfates in the batch to 2.25 kg (in sodium-sulfate equivalent) per 100 kg of quartz sand. Glass melting in this case proceeds without technological complications, similarly to the case where $Na_2O$ is introduced via ammonia soda and sodium sulfate in a ratio of 95.0 : 5.0.

Thus, using nepheline soda with a content of potassium sulfate equal to $0.4 – 1.3\%$ $K_2SO_4$ is present in the batch in such insignificant quantities that its active corrosion effect on the refractory brickwork of the furnace appears improbable. Furthermore, the presence of potassium sulfate in nepheline soda decreases the consumption of expensive sodium sulfate. The glass-melting process using nepheline soda with a soda : sulfate ratio of 99.5 : 0.5 – 95.0 : 5.0 proceeds according to the same technological scheme as using the classical composition of ammonia soda – sodium sulfate for introducing $Na_2O$ in glass. At the same time, such positive effects of melting a soda – sulfate batch as a high-temperature catalytic effect on the clarification of the glass melt and prevention of silica foam formation are preserved.

The quality of nepheline soda is currently significantly improved compared with parameters prescribed by the current GOST 10689–75 standard, judging from results of testing soda of categories 1 and 2.

Thus, the two tested samples of grade 1 soda contain 0.4 and 0.7% $K_2SO_4$, whereas, according to GOST 10689–75, the admissible content of $K_2SO_4$ in this grade of soda is up to 1.5%. The sample of grade 2 obtained for testing contains 1.3% $K_2SO_4$, whereas, according to the standard requirements, the content of $K_2SO_4$ may reach up to 4.4%.

Accordingly, it is recommended that the manufacturer of this material, namely, the Achinskii Alumina Works, develop technological regulations for nepheline soda and pay special attention to decreasing as much as possible the spread in the content of $K_2SO_4$ of particular batches (to stabilize the glass-melting process, it is desirable for this spread not to exceed ± 0.1%).

Thus, nepheline soda corresponding in its quality parameters to the currently manufactured product containing up to 0.7% $K_2SO_4$ can be successfully used along with ammonia soda in production of most industrial glasses. The use of nepheline soda does not lead to technological complications in glass melting and does not endanger the furnace campaign duration.

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